Fine structure in NQR spectra of copper in $YBa_2Cu_3O_{6.0+x}$

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Fine structure has been observed in the nuclear-quadrupole-resonance spectra of copper in the Cu^2 position in $YBa_2Cu_3O_{6.0+x}$ compounds ($x = 0.0$–0.95). This fine structure apparently reflects a sensitivity of the resonant frequency to the extent to which oxygen atoms preferentially fill 04 positions. The intensity redistribution among the various lines with increasing x indicates an increase in the number of pairs of 04 oxygen atoms as the composition goes into the superconducting region.

As the oxygen concentration in the compound $YBa_2Cu_3O_{6.0+x}$ is increased, there is a transition from a tetragonal phase (space group D_{4h}^1 to an orthorhombic phase[1,2] (D_{2h}^1.) At $x \approx 1$, the superconducting transition temperature T_c is observed to have its highest value. It is believed that this transition results from the preferential filling of 04 positions by oxygen. These positions form Cu1–0 atomic chains. The positions 01, 02, and 03, on the other hand (the positions are labeled in accordance with the orthorhombic phase[1]), are filled to the greatest extent throughout the x phase diagram, according to data from neutron diffraction analysis. A study of the nuclear quadrupole resonance (NQR)[3] at $x = 0.0$ and 0.95 has shown that the signal frequency depends on the oxygen concentration as a result of a change in the components of the electric-field-gradient tensor, whose magnitude is determined by the distribution of the charge density near the copper atom. Our purpose in the present study was to learn about the NQR spectra in several $YBa_2Cu_3O_{6.0+x}$ compounds ($x = 0.00$–0.95) in order to determine the particular way in which 04 positions are filled.

Samples with various deviations from stoichiometry in terms of oxygen were synthesized from the $YBa_2Cu_3O_{6.95}$ phase through a reducing heat treatment in a circulation cell with a controlled oxygen pressure p_0. After an isothermal hold at $T = 800$°C and at a given equilibrium value of $p_0(x)$, the sample temperature was lowered at a rate of 1 deg/min. The oxygen pressure above the sample, which simultaneously varied in accordance with the p-T-x diagram, thereby maintained a constant-composition during the cooling. The resulting samples were single-phase samples, according to data from neutron diffraction and x-ray structure analysis. The NQR spectra were recorded by the spin-echo method on an ISSh-2-13 spectrometer at $T = 78$ K over the interval 18–35 MHz. The length of the 90° pulse was $\tau_p = 3$ μs; the interval between the pulses forming the echo was 40–50 μs.

In a previous study[3] for the composition $x = 0.95$, it was shown that the NQR signal of ^{63}Cu at the frequency $\nu = 22.05$ MHz is formed by copper atoms in Cu1 positions, while the NQR line at $\nu = 31.45$ MHz corresponds to Cu2 positions, in agreement with the conclusions reached in Refs. 4 and 5. With decreasing oxygen

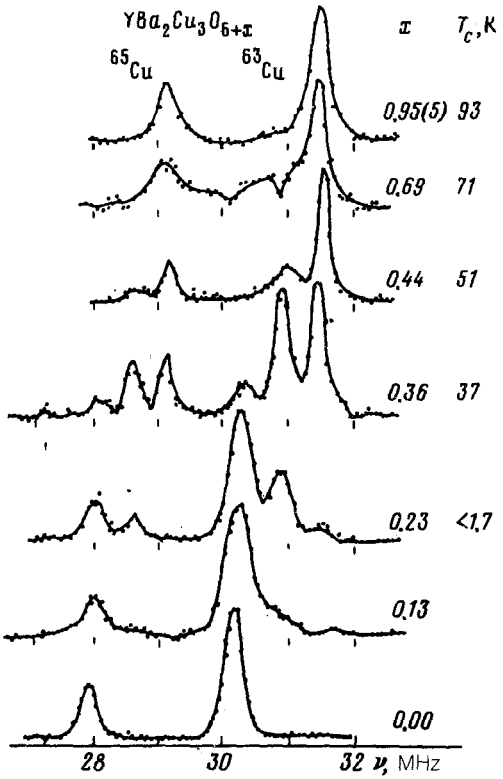

FIG. 1. Nuclear-quadrupole-resonance spectra of copper in Cu2 positions at $T = 78$ K in $YBa_2Cu_3O_{6.0+x}$ samples.

concentration in the Cu1–04 chains, the NQR spectrum in the interval 28–32 MHz becomes more complex (Fig. 1). The spectrum here consists of three uniformly spaced lines of approximately equal width $\delta\nu = 200$–300 kHz. The resonant frequencies of the lines remain constant, within the error of the determination. We observe a redistribution of the line intensities: With a decrease in x, the intensity of the low-frequency line ($\nu = 30.35$ MHz) increases, while the intensity of the central line reaches a maximum at $x = 0.36$. The observed shift of the NQR lines, $\Delta\nu_Q/\nu_Q \approx 0.02$, reflects a change in the magnitude of the electric-field gradient at the given copper nucleus. Since the samples are single-phase samples, and since the 01, 02, and 03 positions are filled, it can be assumed that the equidistant structure in the spectra results from a charge perturbation of the electric-field gradient at Cu2 positions by oxygen atoms filling 04 positions, which are close to the resonant copper atom (Cu2; Fig. 2). In this case the intensities of the various lines in the spectrum are determined by the probability for the filling of 04 positions by oxygen atoms, and each line can be assigned a specific 04–Cu1–04 configuration: I) The frequency 30.35 MHz corresponds to the absence of oxygen atoms from 04 positions. II) The frequency 30.9 MHz corresponds to the presence of a single oxygen atom. III) The frequency 31.45 MHz corresponds to the case in which oxygen atoms fill both of the 04 positions in the nearest neighborhood of the Cu2 copper atom. Figure 3 shows the concentration dependence of the relative

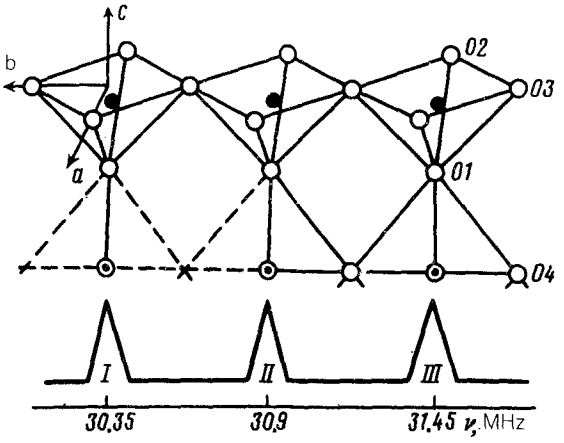

FIG. 2. Various configurations of the oxygen neighborhood of Cu1 copper atoms and their relationship with observed lines in the NQR spectrum of copper in $YBa_2Cu_3O_{6.0+x}$. ●—Cu2; ⊙—Cu1; ○—0 positions.

intensity I of line III, which is proportional to the probability for the formation of oxygen 04 pairs in the nearest neighborhood of the Cu2 atoms. The value of this intensity at $x = 6.2$–6.7 is substantially higher than that calculated under the assumption of a statistical distribution of oxygen atoms among 04 positions. For a binomial distribution we would have $I \sim x^2$. The apparent explanation is that configuration II, with a single oxygen atom in Cu1–04 linear chain, is less stable. Also shown in this figure is the concentration dependence of T_c found for these samples. Its behavior is close to that published in Ref. 2. A comparison of the dependence $I(x)$ with $T_c(x)$ leads to the conclusion that the superconducting state arises in the series $YBa_2Cu_3O_{6.0+x}$ in a region in which there is a sharp increase in the number of oxygen pairs in the nearest neighborhood of the Cu1 copper atoms.

While preparing this paper for publication, we learned of Lütgemeier's report[6] of a Zeeman splitting of the NQR line at the frequency 30.2 MHz at $x = 0.15$. That line had a width, $\delta\nu \approx 1$ MHz, substantially greater than that in our own samples. Lütgemeier linked the splitting with induced dipole fields from antiferromagnetically or-

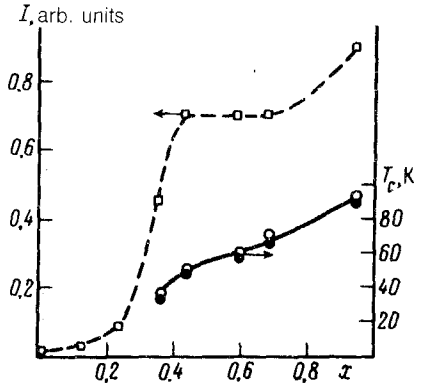

FIG. 3. Concentration dependence of (1) the relative intensity I of an NQR line ($\nu_Q = 31.45$ MHz) and (○,●) the superconducting transition temperature T_c in the compound $YBa_2Cu_3O_{6.0+x}$. ○—According to measurements of the resistivity; ●—according to measurements by an induction method.

dered magnetic moments in Cu2 positions. The line $\delta\nu = 30.2$ MHz was attributed to positions (I in Fig. 2) with an approximately axial electric-field-gradient tensor. We did not observe a splitting of this sort in any of the nonsuperconducting compositions. This result agrees with data from neutron-diffraction studies, in which attempts to detect magnetic scattering peaks in a sample with $x = 0.0$ did not lead to a positive result. We wish to thank V.I. Voronin for furnishing the results of a neutron-diffraction analysis before their publication.

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